

University of Groningen

## Defect ferromagnetism in ZnO and SnO<sub>2</sub> induced by non-magnetic dopants

Akbar, Sadaf

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

2017

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Akbar, S. (2017). *Defect ferromagnetism in ZnO and SnO<sub>2</sub> induced by non-magnetic dopants*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

## Summary

The objective of this summary is to place the entirety of our results in a general and, as far as possible, consistent conceptual framework. To this end we recall that the principal conclusion derived from various earlier studies was that suitable defects (*e.g.* cationic vacancies) in ZnO and SnO<sub>2</sub> systems can enable ferromagnetic behaviour even for small dopant concentrations. We concluded that the structural, morphological, electronic, magnetic, optical and electrical properties are highly sensitive to the addition of non-magnetic dopants and this sensitivity again seems to derive from how the dopants affect the relative concentration of defects. A crucial question to this end was how to describe the specific role played by non-magnetic defects in stabilizing and enhancing ferromagnetism in these oxide systems.

The first experimental chapter of this dissertation (Chapter 3) illustrates the behaviour of carbon-doped ZnO thin films with *n*-type conductivity prepared by electron beam evaporation and by pulse arc discharge. We conducted comprehensive magnetic, electronic (XPS), optical and Hall effect measurements on this system and analyzed the variety of data in relation to the latest models. By correlating the results of these different measurements we excluded the possibilities of various models and established the role of zinc vacancies as the source of ferromagnetism and the role of carbon as stabilizing these intrinsic defects. While a zinc vacancy is generally a high energy defect, its formation is relatively easier on surfaces or in the presence of a suitable dopant. The presence of C in a higher valence state would generate an excess of electronic charge and the excess charge can be compensated by the generation of zinc vacancies. Zn vacancies lead to unpaired O electrons in their immediate neighbourhood, which provide the moment, while the coupling between these unpaired O 2*p* electrons can lead to the development of room temperature ferromagnetism. XPS measurements gave evidence for C substitution at zinc sites and were consistent with the formation of C-O bonds. In a follow up to this work (chapter 4), we studied the effects of different preparation conditions, *e.g.* sintering in a reducing environment and in nitrogen, on ferromagnetism in C-doped ZnO, albeit in bulk samples. The enhanced saturation magnetization of samples sintered in a reducing atmosphere suggests that the presence of oxygen vacancies is important for the ferromagnetism of C-doped ZnO bulk system. Samples sintered in nitrogen atmosphere showed instead diamagnetic behaviour. N substituting for O in the lattice acts as an acceptor and can compensate for existing O vacancies, thereby decreasing the defect density and the concentration of conduction electrons. All carbon

related defects ( $C_{Zn}$ ,  $C_i-C_i$ ) and oxygen vacancies give electrons to the system and these itinerant electrons are important in mediating the ferromagnetic interactions in C-ZnO, however sintering in  $N_2$  depletes these carriers. Band gap measurements of C-doped ZnO powder revealed that the band gap shrinks with increasing carbon concentration, suggesting the introduction of donor levels close to the bottom of conduction band, which lower the band gap energy.

The second part of this PhD project was focused on studying ferromagnetism in another wide band gap semiconductor,  $SnO_2$ , doped with non-magnetic dopants, *i.e.* Zn and Li. Chapter 5 demonstrated the complex interplay between nanostructures, defect formation and consequent ferromagnetism. A room temperature ferromagnetic and paramagnetic response was observed for all compositions of  $Sn_{1-x}Zn_xO_2$  nanoparticles, with a maximum for  $x=0.04$ . Structural and XPS studies confirmed that the enhancement of ferromagnetic response is strong in the region where zinc is incorporated substitutionally and the oxygen vacancy concentration is relatively small. This is explained as zinc substituting for Sn acts as a hole dopant for the O  $2p$  bands, while oxygen vacancies counteract the effect by introducing electrons and reducing the hole concentration, thereby degrading the ferromagnetic response. There is a pronounced paramagnetic response, which we understand as originating from the singly charged oxygen vacancies and possibly also from magnetic defects that are too far apart to stabilize ferromagnetism. We also found that the morphology of the nanostructures varies with zinc concentration and the stronger ferromagnetic response came from nanostructures with nanoneedles on their surfaces. These nanoneedles were seen to consist of (110) and (101) planes which are important in stabilizing the ferromagnetic defects. We explained the observed trends in the light of recent computational studies that discuss the relative stability of ferromagnetic defects ( $V_{Sn}$ ) on these surfaces and the role of oxygen vacancies in degrading ferromagnetism via the increase of the free electron concentration. This part of our work is the most significant contribution to the very complex field of defect ferromagnetism. Thus ferromagnetism due to defects formed in Zn-doped  $SnO_2$  is the result of three factors, namely, the stabilization of  $V_{Sn}$  and  $Zn_{Sn}$  defects; the presence of oxygen vacancies required for charge compensation and finally morphological variations that in turn affect both preceding factors by controlling the stabilization energies of various defects.

Raman spectra, photoluminescence and band gap of undoped  $SnO_2$  and of  $Sn_{1-x}Zn_xO_2$  ( $x=0.02, 0.04, 0.06, 0.10$ ) nanostructures were studied in chapter 6. In addition to other features the

observed infrared active surface mode at  $556\text{ cm}^{-1}$  and its blue shift with increasing Zn concentration were ascribed to the effects of oxygen deficiency. Photoluminescence results testify to the presence of singly ionized oxygen vacancies.  $V_0^+$  appear as the recombination centres for the luminescence process, and the PL intensity associated with this defect increases in the zinc-doped system. We correlate the presence of these defects with the paramagnetic response of Zn-doped  $\text{SnO}_2$ . The observed trend of decreasing the band gap with Zn dopant concentration may be due to structural defects introduced by the  $\text{Zn}^{+2}$  dopant such as tin interstitials and oxygen vacancies, which give rise to the electronic states in the gap close to the conduction band.

The last experimental chapter of this dissertation (Chapter 7) demonstrates the role of Li as a ferromagnetic defect in  $\text{SnO}_2$  nanoparticles, which was seen to be less effective as compared to Zn. Li-doped nanoparticles showed ferromagnetism (in addition to a paramagnetic contribution) in the range of particle size 16-51 nm, while other Li-doped compounds below and above this particular range of sizes, including undoped  $\text{SnO}_2$ , are diamagnetic. XPS data shows the presence of  $\text{Li}_{\text{Sn}}$  and  $\text{Li}_i$  defects. Li prefers to occupy the interstitial positions at low concentration, and substitutes Sn at moderate concentrations along with  $\text{Li}_i$ . Comparing the variation in magnetic moment with Li concentration, we note that the moment is large for compositions where XRD and XPS indicate significant concentrations of Li substituting for Sn in addition to those occupying interstitial sites. Ferromagnetic ordering in Li-doped  $\text{SnO}_2$  nanoparticles is mainly due to the holes created by  $\text{Li}_{\text{Sn}}$ . Meanwhile,  $\text{Li}_i$  acting as electron donors may combine with the holes induced by  $\text{Li}_{\text{Sn}}$  and decrease the ferromagnetism. Beyond a certain limit, at the higher concentration of Li,  $\text{Li}_i$  prevail and negative effects on the ferromagnetism appear along with the paramagnetic contribution. We note however that ferromagnetism - albeit weak - is present in compositions where interstitial Li is clearly dominant. This suggests that in addition to the role played by substitutional Li as a FM defect, both substitutional and interstitial defects may be supporting ferromagnetism by forming a stable magnetic defect complex that includes in addition a Sn vacancy. Our observation of the presence of both substitutional and interstitial defects could be an indicator of such a complex defect.

Given the versatility of the preparation of metal oxide samples, this work opens the way for further development of materials with defect mediated ferromagnetism by incorporation of

different kinds of non-magnetic dopants and therefore represents a new step towards the realization of spintronics applications.